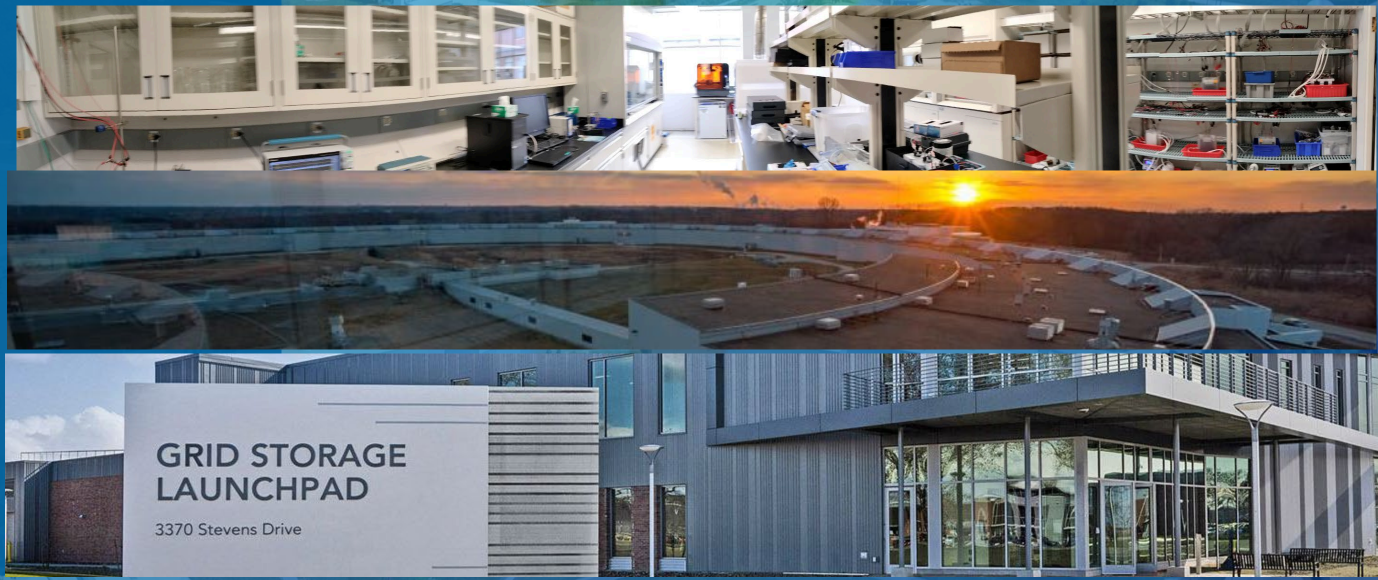
AUGUST 7, 2024

ADAPTING LEAD ACID BATTERIES TO LDES: NEW ANALYSIS TOOLS, MATERIALS, AND CELL DESIGN



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OUR APPROACH

Identifying the microscopic origins of macroscopic failure modes

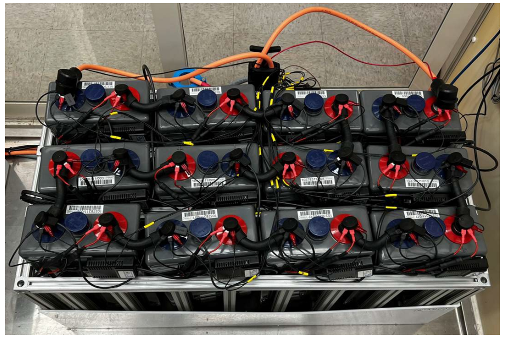
Lead acid batteries are often evaluated using a top-down approach:

Cell/battery cycling: Average properties Q, I(t)/Q(SOC), V(t)

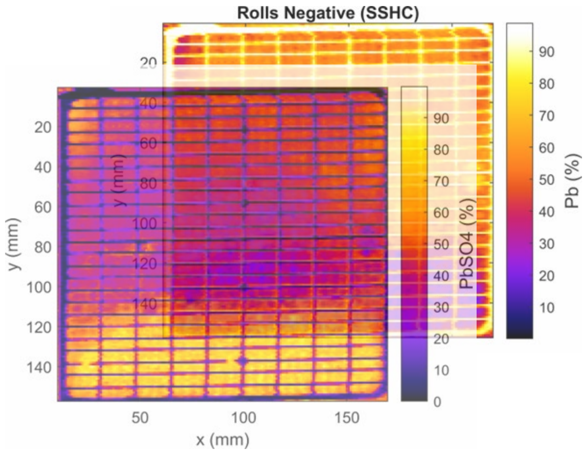
~mm: Continuum level challenges: diffusion, stratification, impedance

~µm: Particle/pore scale changes: surface area, tortuosity, local pH/ solubility

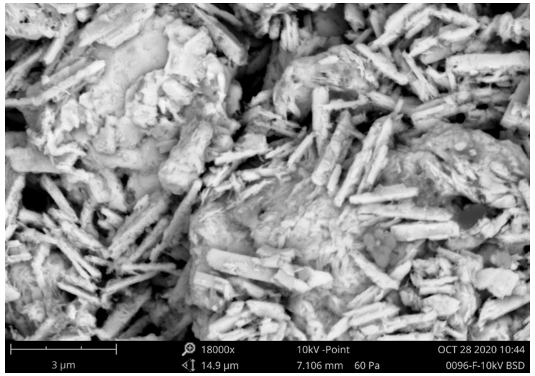
~nm: Interfacial nucleation, lattice defects



Cycling at PNNL

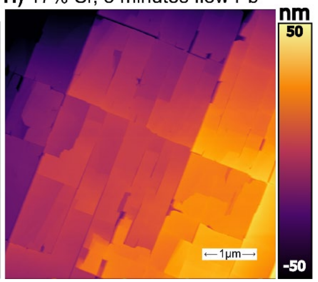


XRD mapping of end-of-life negative plates at APS

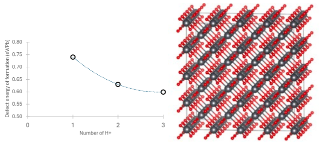


SEM from paste electrode species

AFM during $PbSO_4$ growth on $(Ba,Sr)SO_4$ 210



Lattice constant changes and DFT calculations



Optimized cycling parameters and electrochemical signatures for emerging failure modes

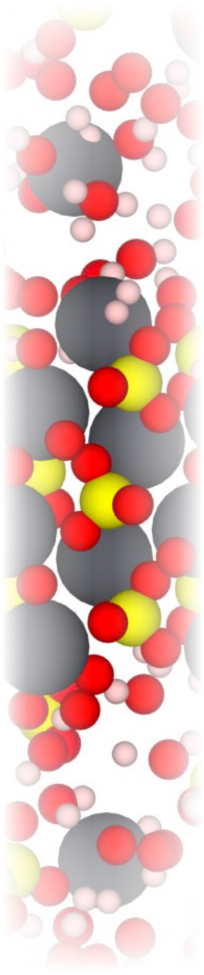
Managing stratification, preserving alkaline phases: formation and cycling, acid management for higher utilization

Controlling $PbSO_4$ and PbO_2 ripening: managing crystallographic defects to extend cycle life

Bottom-up: can we ***design*** lead acid batteries knowing the atomic-scale factors that drive cycle-life?

OVERVIEW

ANL & PNNL studies



Molecular-scale Picture: past and present publications

Negative electrode:

- Legg 2023: $PbSO_4$ nucleation on $BaSO_4$ 001
- Campbell 2024 (submitted): $(Ba,Sr)SO_4$ materials, 210 surface
- Knehr 2024 (submitted): Role of $Pb/PbSO_4$ morphology on DCA

Positive electrode:

- Kinnibrugh 2024: Pb_2O_3 and Pb_3O_5 crystal structure, spectroscopy
- Garcia 2024 (submitted): DFT of lattice defects in α, βPbO_2

Electrolyte:

- Kinnibrugh 2022: x-ray scattering - structure of sulfuric acid solutions
- Bazak 2021: NMR of sulfuric acid

Future: new characterization, materials and cells for LDES

New characterization tools

- ANL + EPM: Electrode + electrolyte mapping
- ANL, PNNL: Operando microscopy of $PbSO_4$ nucleation and growth
- ANL: Acoustic feedback on commercial batteries

New Materials

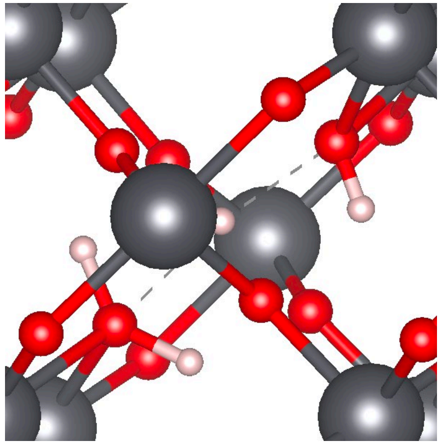
- PNNL + EPM, ANL: evaluation of “strain engineered” nucleation additives

New Cell Design and testing protocols

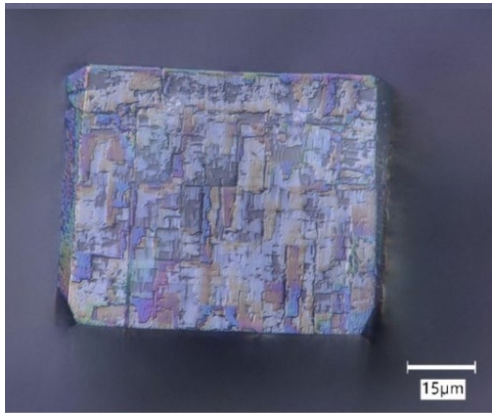
- PNNL: Large scale battery testing, Grid Storage Launchpad
- ANL: Modified cell and electrolyte design for commercial electrodes

OUTLINE

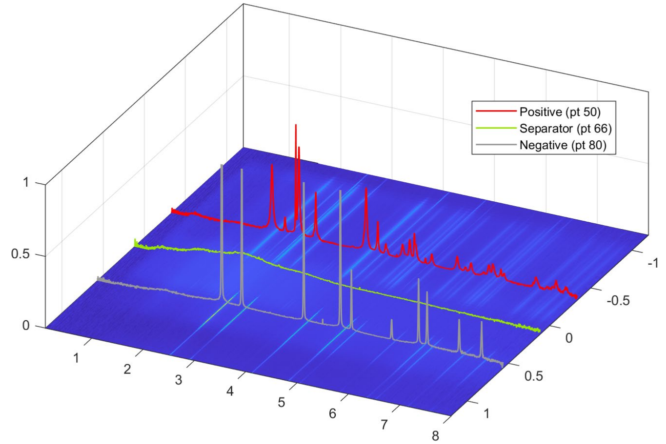
Lead acid for LDES: a bottom-up approach



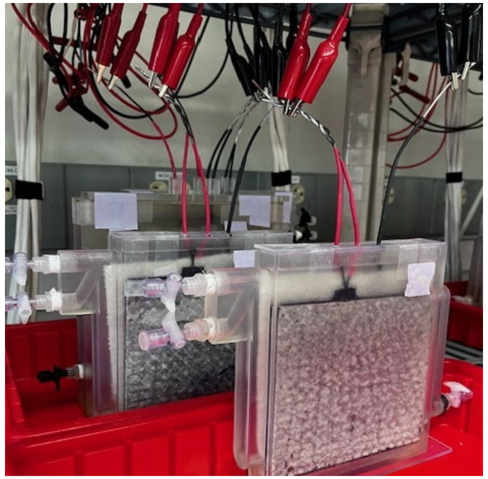
Highlight 1
DFT/NMR/XRD: lattice defects in PbO_2



Highlight 2
In situ microscopy: strain-engineered nucleation additives



Highlight 3:
Depth profiling electrode and electrolyte species during formation



Highlight 4:
Cycling results from PNNL and ANL

Atomic scale | Particles | Electrodes | Cells/batteries

HIGHLIGHTS #1: DEFECTS IN LEAD OXIDES

PbO_x and $Pb_{1-x}O_2H_y$

Defects in lead oxides

- Nonstoichiometric oxides are intrinsic to lead acid batteries:
  - FY23: PbO_x intermediates ($PbO_{1.5}$, $PbO_{1.67}$) are key part of "corrosion layer" (Kinnibrugh et al. 2024): driven by oxygen vacancies: PbO_{2-x}
  - Previous neutron scattering: electrochemically grown PbO_2 often has *Pb* defects that are charge-balanced by interstitial protons: $Pb_{1-x}O_2H_{4x}$
  - Defect concentration correlates with battery state-of-health, i.e. end-of-life PAM has ripened, stoichiometric (defect-free) PbO_2.

Lattice "defects" are good!

Necessary for electronic conductivity in PbO_2 active material and corrosion layer.

Strain from defects inhibits PbO_2 grain ripening.

We are currently working on the following questions:

DFT: what is the energy cost of forming Pb and H defects?

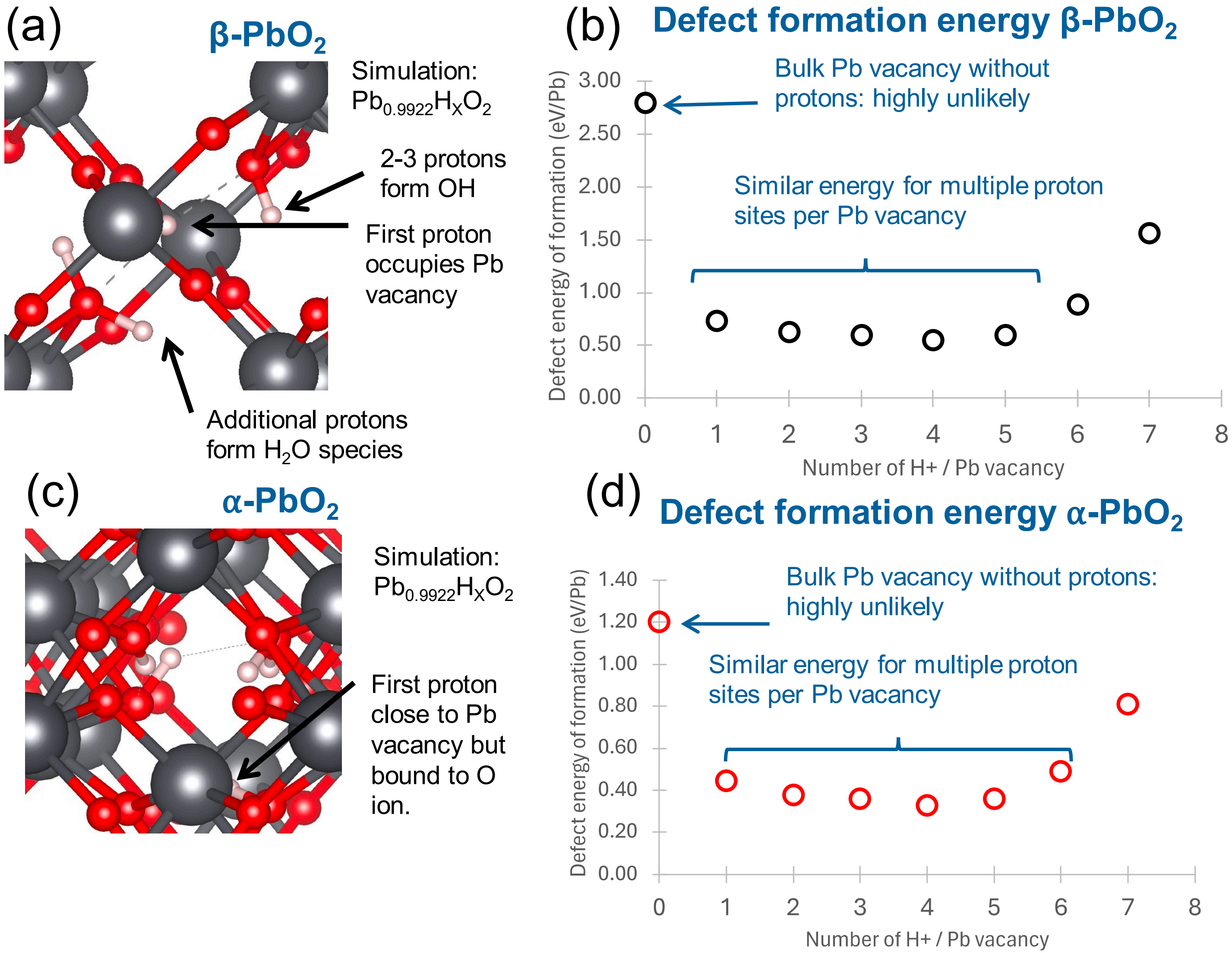
NMR: What is the local environment of the proton site?

XRD/neutrons: How does this affect the overall crystal structure of PbO_2 ***during*** cycling?

THEORY

Predictions

- Thermodynamics: relatively low energy barriers for lead vacancies in both α- and β-PbO_2.
  - H$^+$ concentration is variable, likely varies during cycling with potential.
  - Defects give higher electronic conductivity.
  - **Defects favored at high potential and high pH (low SG)**
- Kinetics (AIMD):
  - Defect energetics smaller at surface than in bulk: likely a growth defect
  - H$^+$ mobility much higher in β-PbO_2 than α-PbO_{2d}



$$\Delta G_{tot} = \Delta G_{rxn} - \mathrm{eU_{SHE}} - \mathrm{k_B TpH}$$

Can this be changed via strain or dopants?

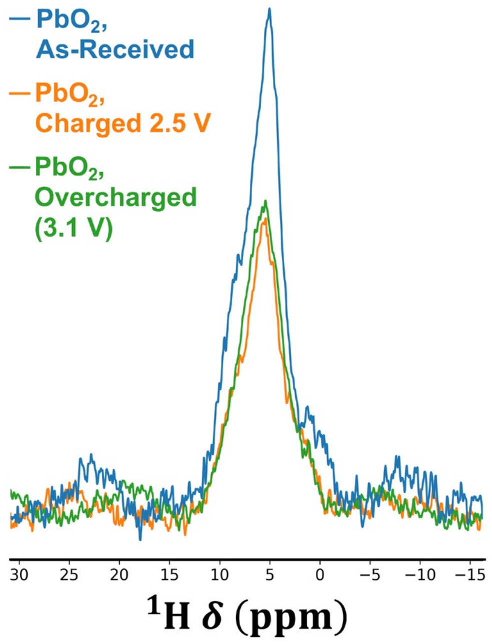
Lower energy at higher potential

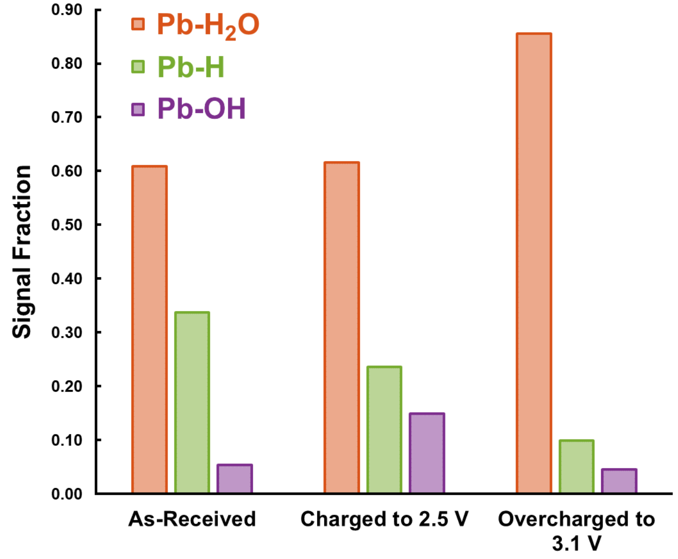
Lower energy at higher pH

SOLID-STATE NMR

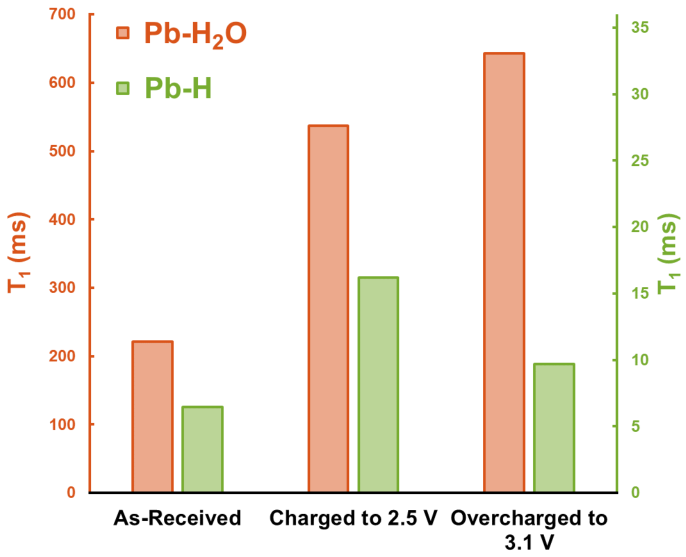
Initial Results Show ^1H PbO_2 Signals, Evolution with Charging

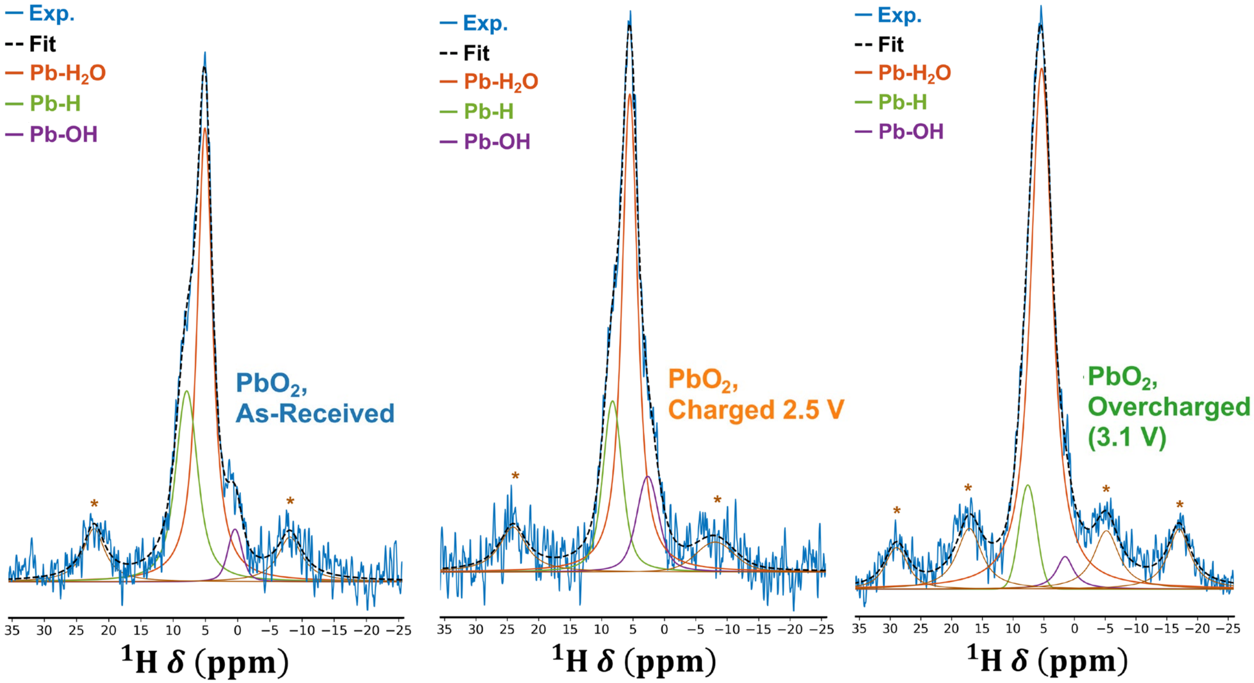
- PbO_2 samples exhibit 3 ^1H signals, with chemical shifts consistent with adsorbed H_2O, a $Pb_{1\text{-}x}OH_x$ bulk defect, and Pb–OH hydroxyls
- The proportion of ^1H defects steadily decreases on going from as-received, to 2.5 V charge, to 3.1 V overcharge, with a larger hydroxyl population at 2.5 V and larger fraction of water-like protons at overcharge





- Reduction of ^1H defects with charging correlates with longer ^1H T_1 relaxation (i.e. reduced electronic conductivity)





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HIGHLIGHT #2: OPTICAL AND ATOMIC FORCE MICROSCOPY GUIDING MATERIAL DESIGN

$PbSO_4$ NUCLEATION

AFM: $PbSO_4$ on $(Ba,Sr)SO_4$

$BaSO_4$ is a common nucleation additive in lead acid batteries.

- Barite is isostructural with $PbSO_4$ and insoluble.

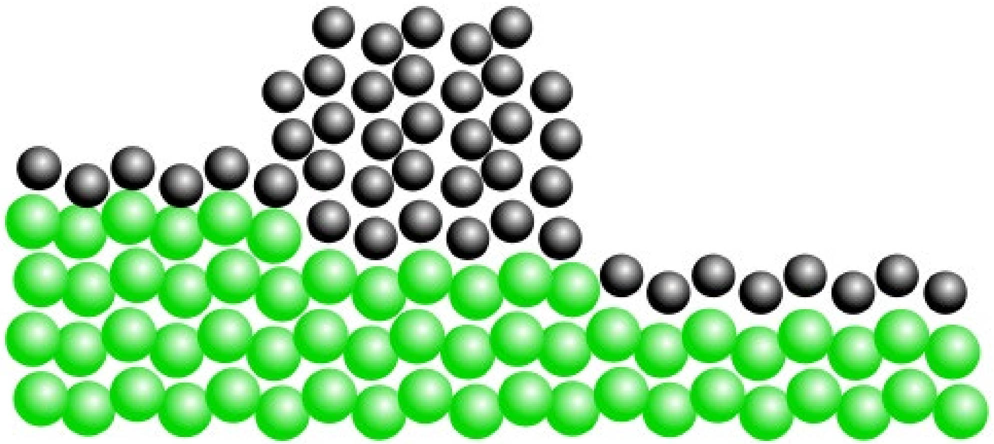
Our previous work (Legg 2023) showed that lattice strain between $PbSO_4$ and $BaSO_4$ actually inhibits epitaxial growth on 001 surfaces.

Can we strain-engineer barite by incorporating Sr for enhanced nucleation?

High strain (traditional barite)

Stranski Krastanov Growth

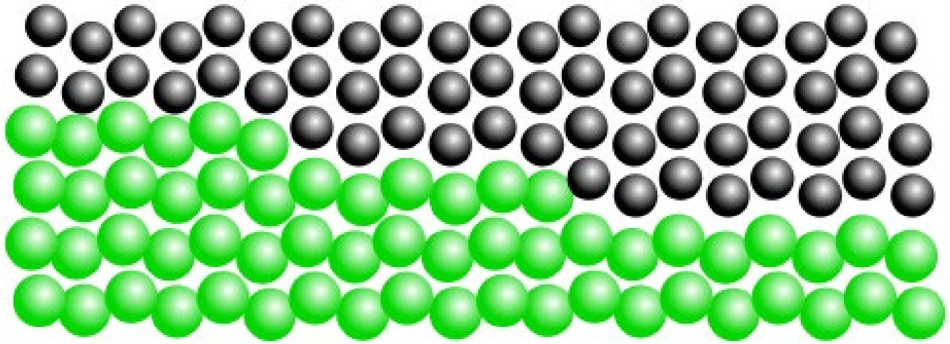
(Frustrated islands over monolayer)



Low strain (engineered barite)

Frank-Van der Merwe Growth

(Layer by layer)

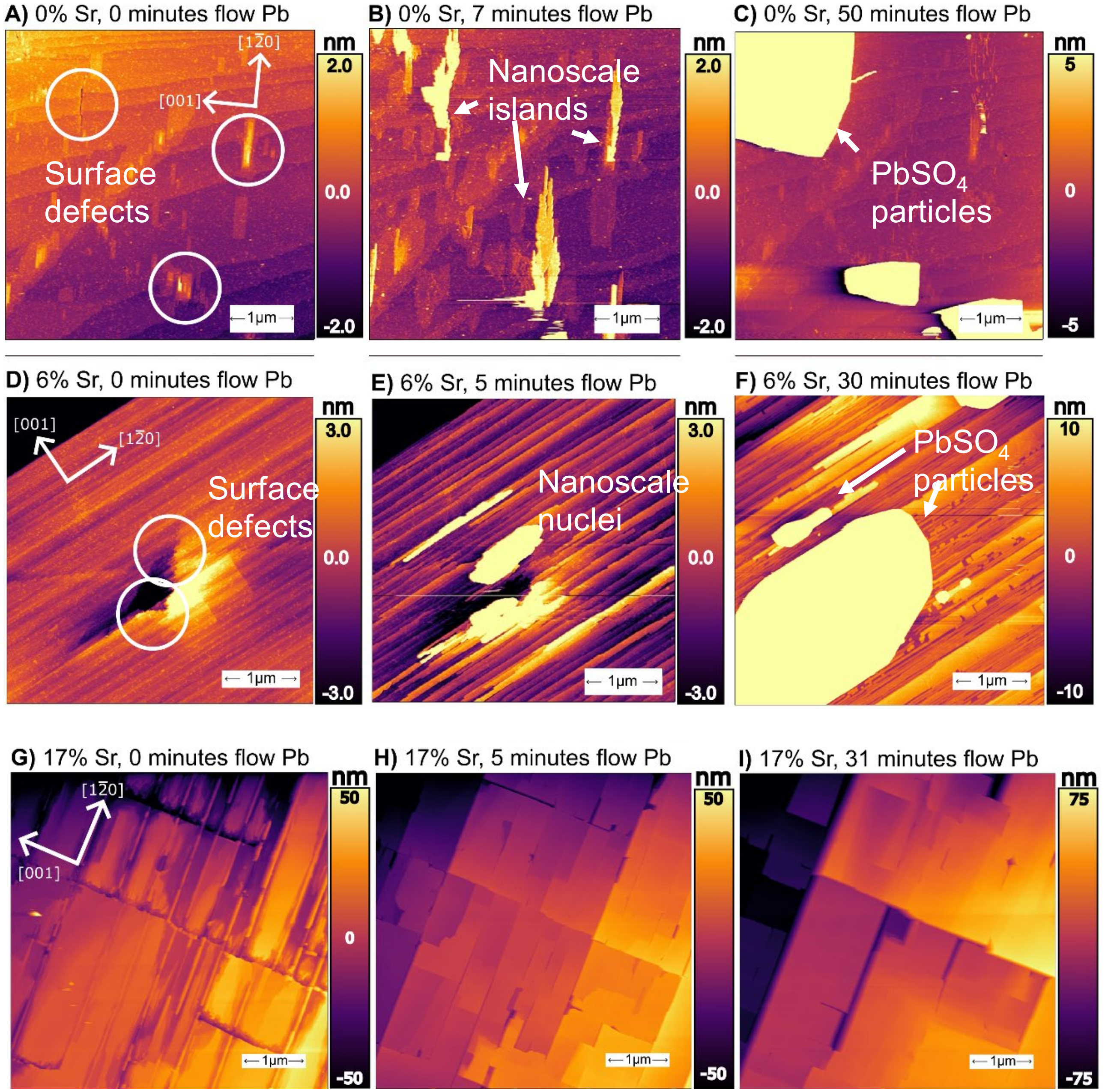


IN SITU AFM

210 surface

In situ AFM of $BaSO_4$ (210) surfaces during discharge conditions show effect of Sr content on $PbSO_4$ growth.

- Pure barite (0% Sr): surface defects nucleate islands that grow into ‘bulk’ $PbSO_4$ particles.
- Lightly doped (6%Sr): defect-nucleated island growth
- Heavily doped barite (17%Sr): Initial pitted surface eventually covered by layer-by-layer $PbSO_4$ growth



OPTICAL MICROSCOPY

PNNL, ANL projects

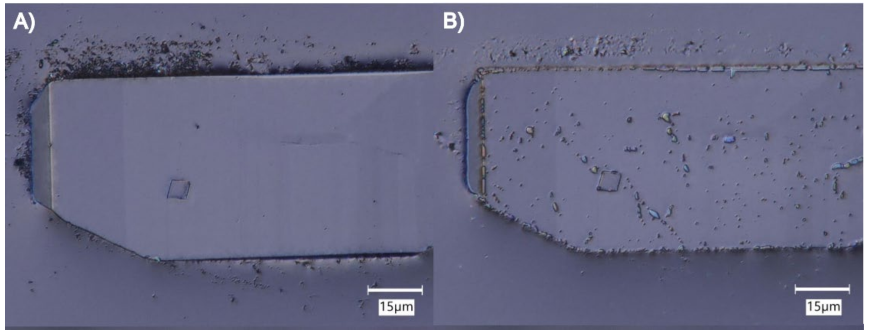
- High resolution optical microscopy confirms different growth modes over entire particle.

Future:

- Test new additives in negative paste formulations (East Penn Manufacturing)
- Study reactions during cycling using new in situ electrochemical cells.
- ANL: developing holographic microscopy for sub-nm height resolution

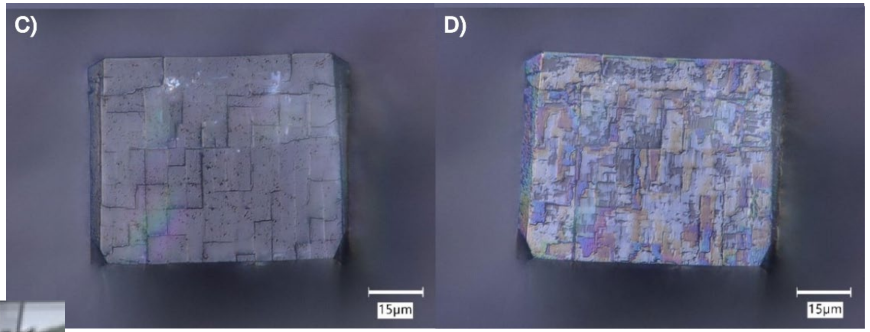
Pure Barite (0% Sr)

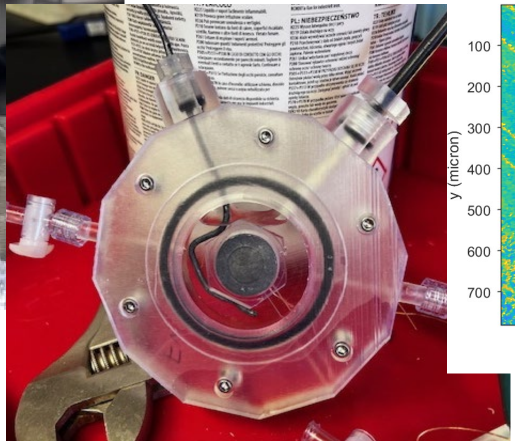
$PbSO_4$ nuclei are scattered sparsely across surface on defects, and at specific crystallographic features (i.e. facet edges).

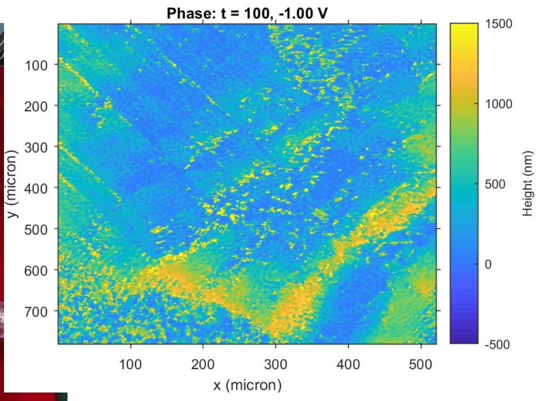


Heavily-doped barite (17% Sr)

No particles are observed. Iridescent pattern indicates thin film of $PbSO_{4,}$ growth, distributed evenly across surface.







Electrochemical cells developed at ANL for digital holographic microscopy

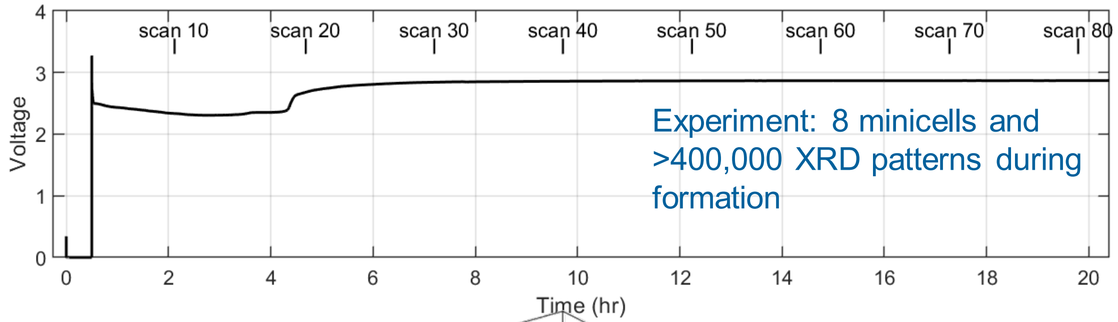
HIGHLIGHT #3:
DEPTH PROFILING ELECTRODE AND ELECTROLYTE SPECIES

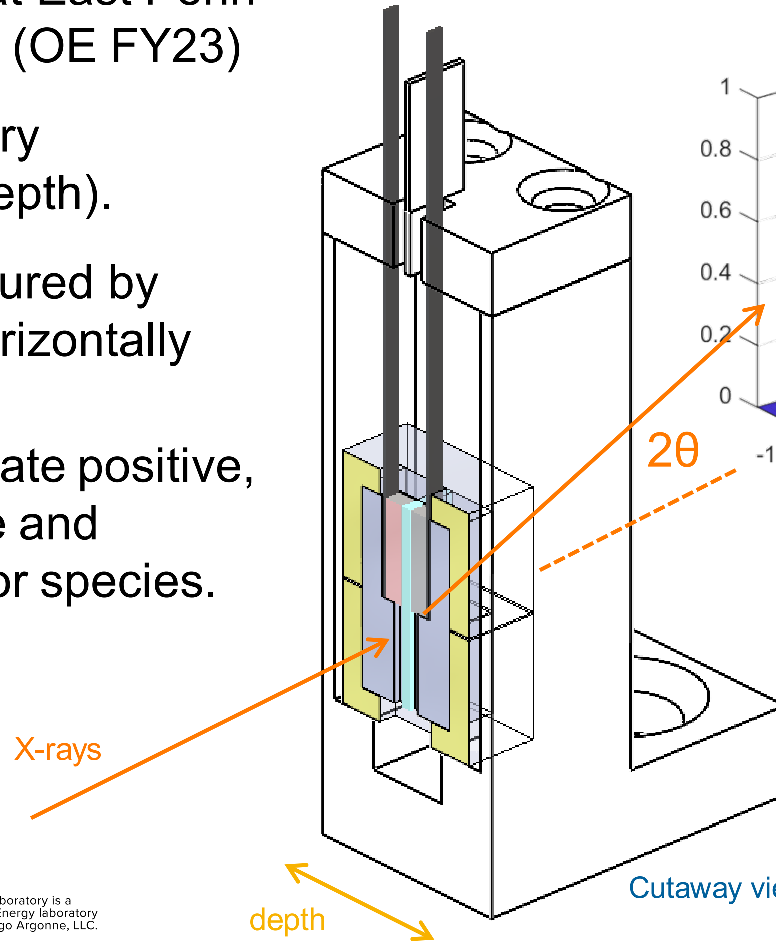
DEPTH PROFILING

Rietveld refinement of electrode *and* electrolyte species

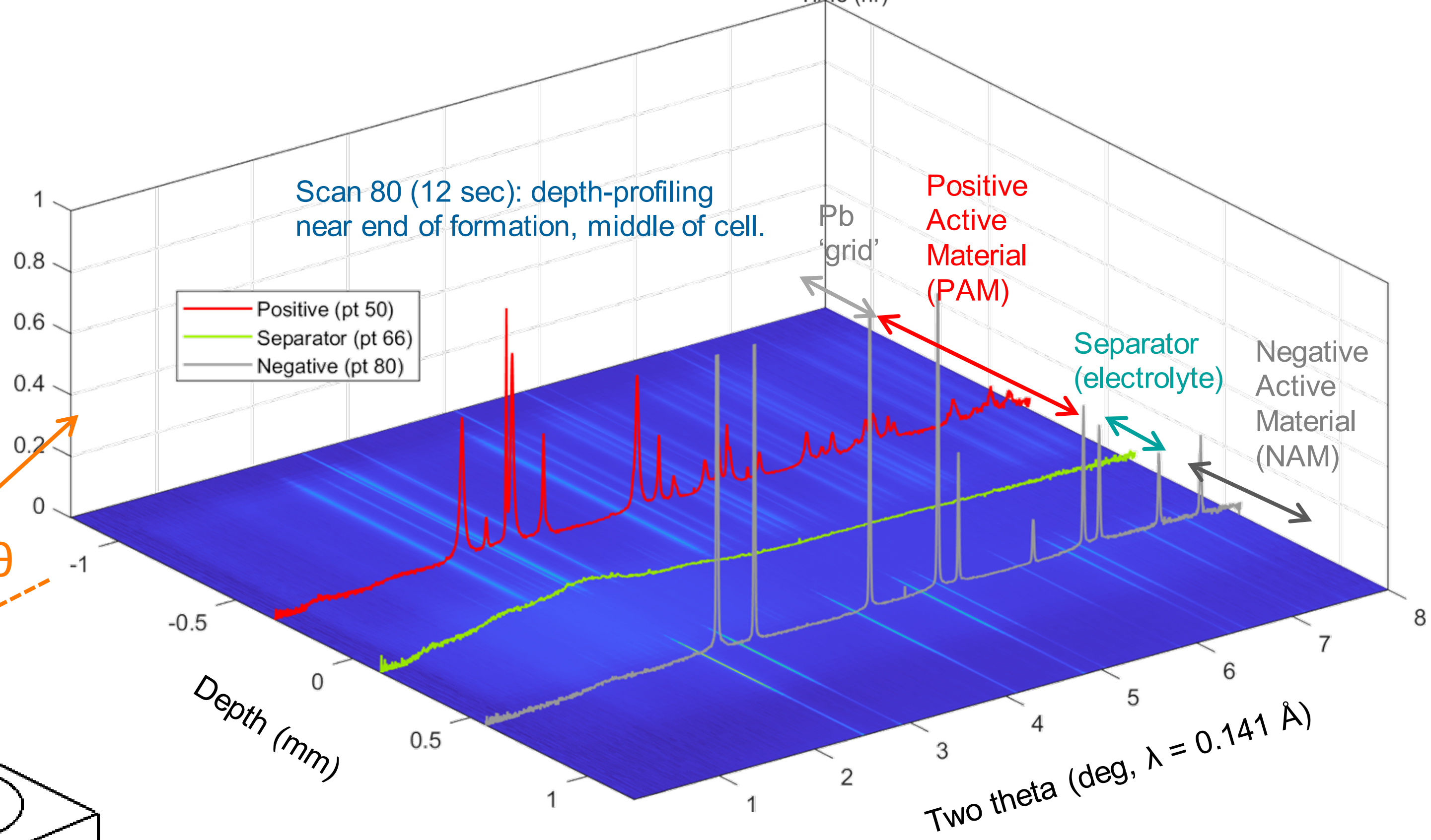
“Minicells” developed by collaborators at East Penn Manufacturing (OE FY23)

- Planar battery (1D along depth).
- Depth measured by scanning horizontally through cell.
  - Can isolate positive, negative and separator species.





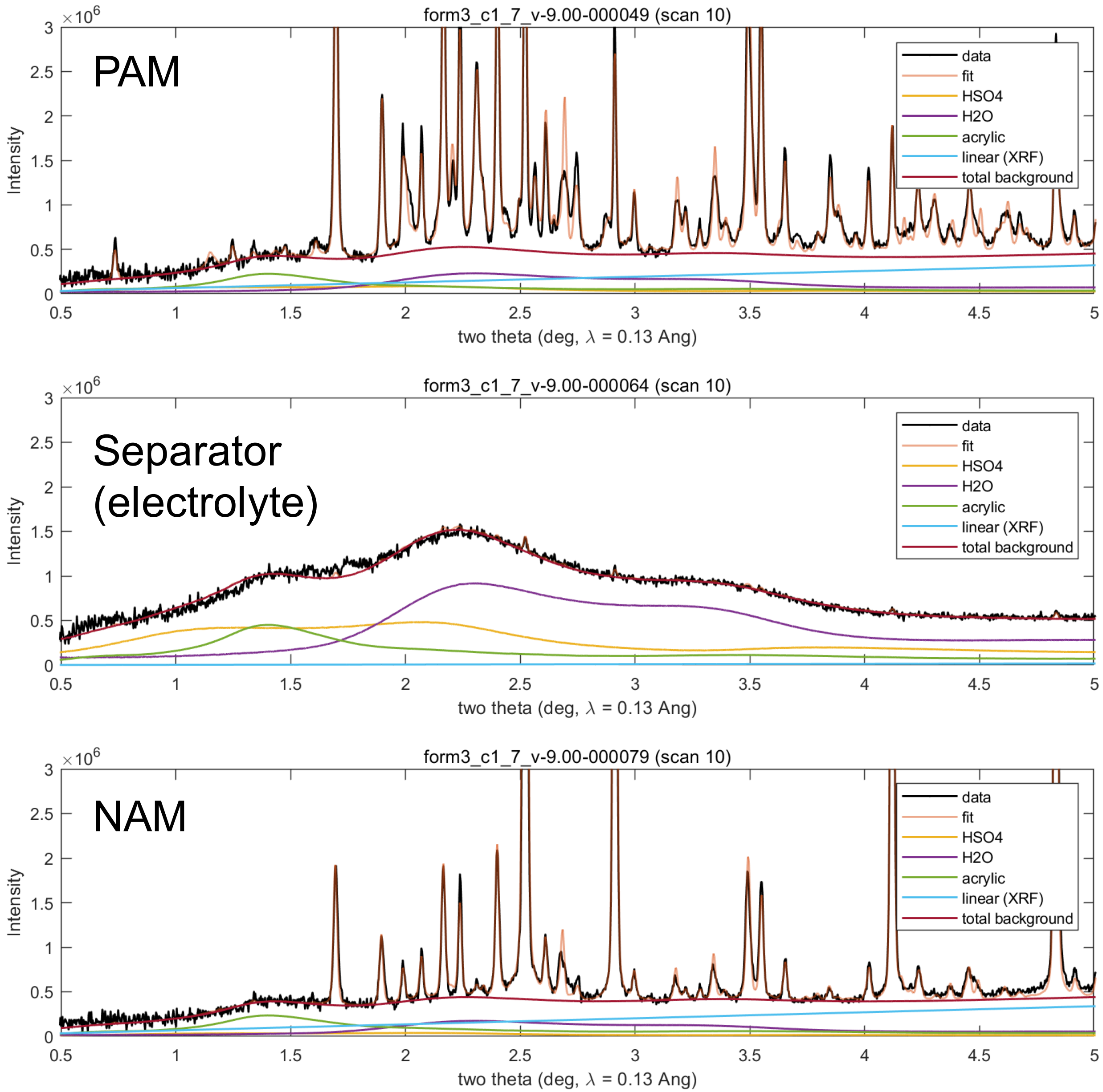
Cutaway view of minicell (CAD)



TOTAL X-RAY SCATTERING

Rietveld refinement of electrode *and* electrolyte species

- FY24: Kinnibrugh/Fister: integrated TOPAS into existing x-ray mapping code.
  - Co-refine 8 crystalline species with 4 non-crystalline components (acid, plastic species).
  - H_2O and HSO_4 from Kinnibrugh 2022.
  - Improvement over previous approach (OE peer review FY22) which refined background and diffraction separately.
- FY24 case studies using minicells:
  - Formation with varying acid concentration
  - Dynamic charge acceptance (not shown)



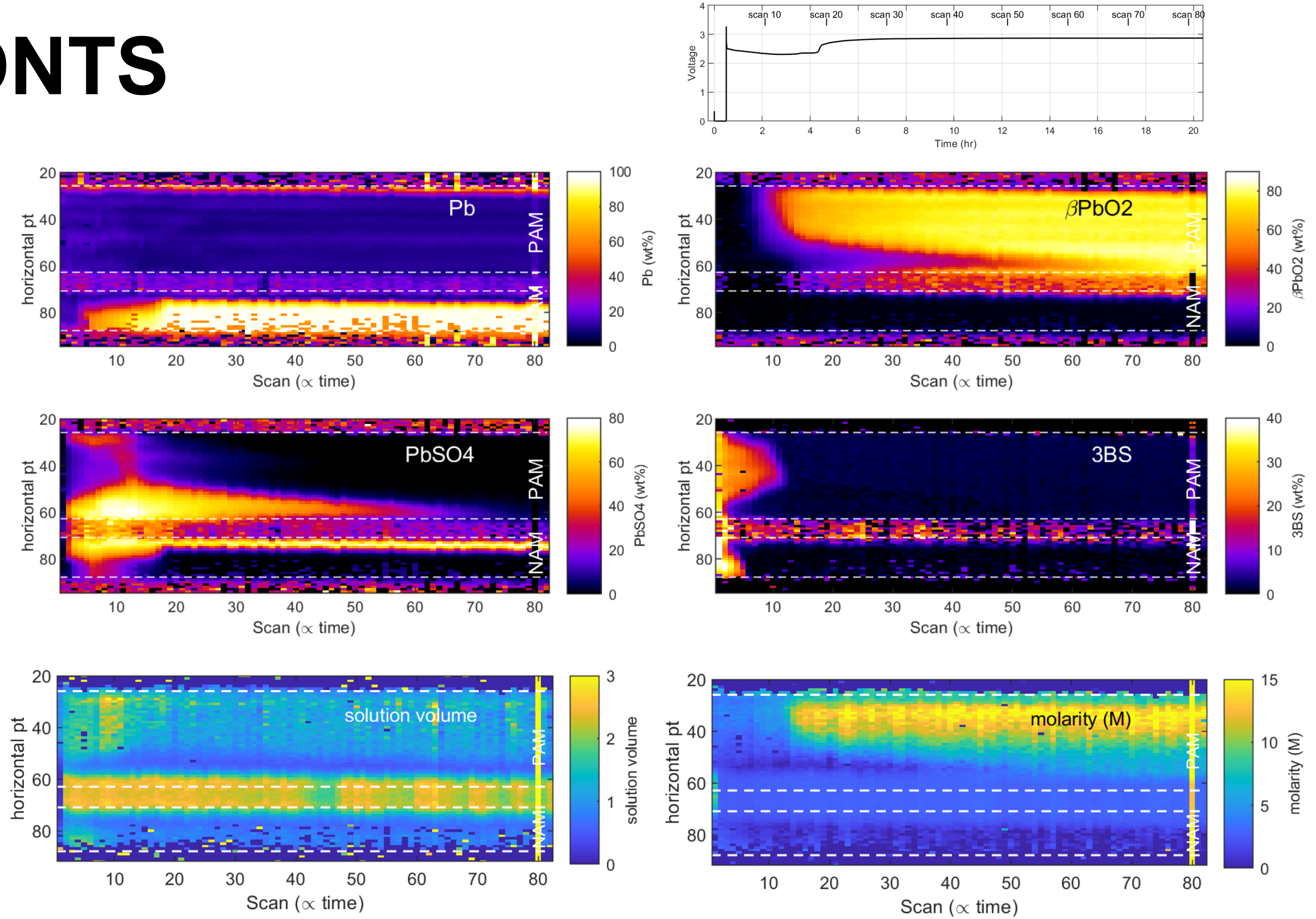
2D MAPS: REACTION FRONTS

Depth x time

Two observed phase fronts:

- Basic phases (3BS, PbO, etc) convert to $PbSO_4$ near separator and slowly convert to Pb, PbO_2.
- Rapid, direct conversion of basic phases to PbO_2 and Pb in interior of electrode. This leads large changes in internal acid concentration.

- **Takeaway**: managing local acid concentration could be key toward improving formation and cycling…



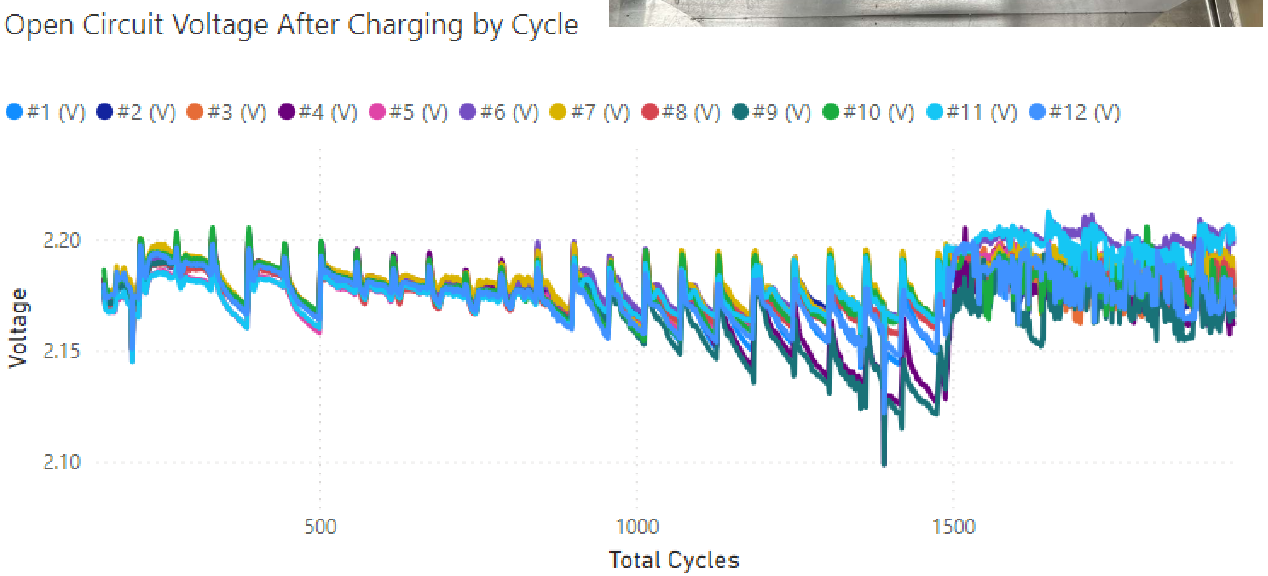
Select electrode and electrolyte species from cell1 (1080 formation, middle of cell)

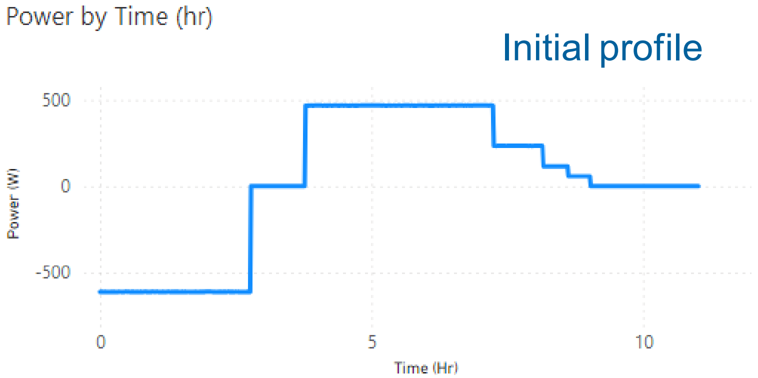
HIGHLIGHT #4: REDESIGNED CELL ARCHITECTURES AND NEW FEEDBACK TOOLS

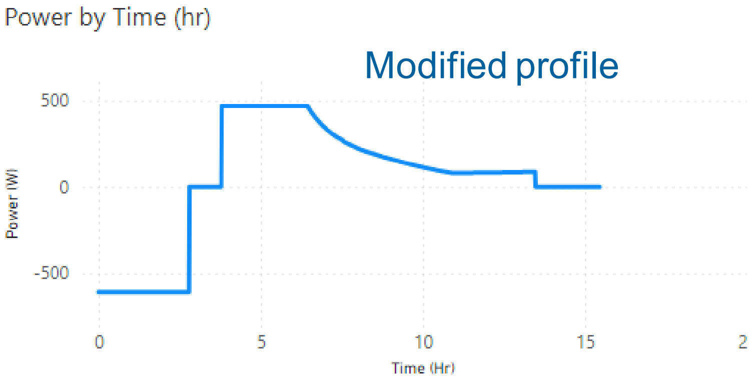
PNNL: LARGE SCALE BATTERY TESTING

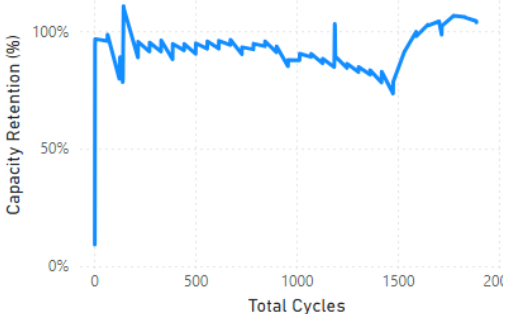
Tubular gel batteries: designed for cycle life

- Commercial gel VRLA battery pack, started 3.5 years ago at PNNL.
  - 50%DOD cycling constant power discharge 610W (Currently 2.8 hr discharge time)
  - Constant power recharge up to 1477 cycles (using a current cutoff).
  - Added a 2.8A constant current step and regained capacity.
  - **Still maintaining 100% capacity at 2000 cycles.**









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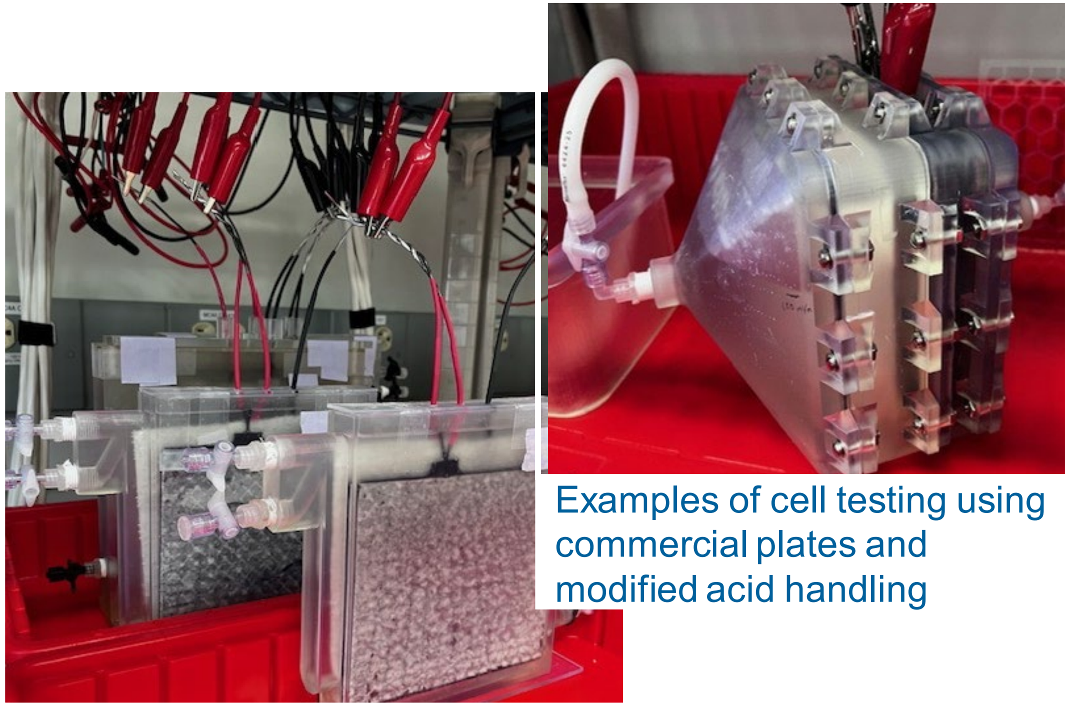
CHALLENGE

Improving cycle life, utilization of SLI batteries

- Lead acid batteries for stationary applications can reach thousands of cycles, but have higher up-front costs.
  - Tubular gel (last slide): $360/kWh
- Upfront cost of mass-produced lead acid batteries for automotive (SLI) applications is much cheaper:
  - **Flooded: ~$65/kWh***
  - AGM/EFB: ~$130-160/kWh*
- SLI batteries are acid-limited in their capacity
  - Can we unlock more capacity with…more acid?
  - Do batteries cycle better in lower specific gravity (SG) acid? (low SG = higher Pb^{2+} solubility, more defects)
- Our approach: repackage SLI plates in modified 2V cell architecture. (70 cells and counting)

*Avicenne market analysis (ELBC2021)

Aqueous Battery Laboratory (opened Aug 2023, ANL): cell analysis, manufacturing, and testing for lead acid, iron, and zinc chemistries for LDES applications.

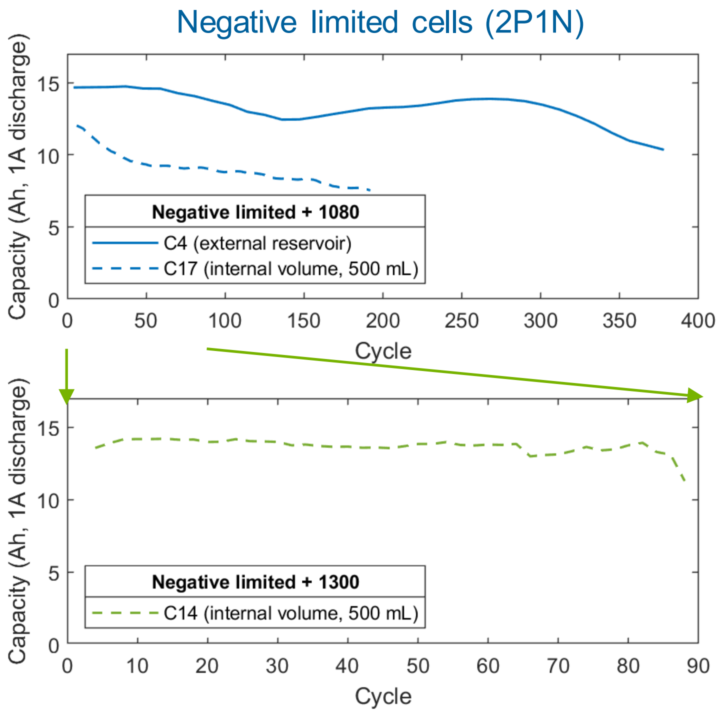


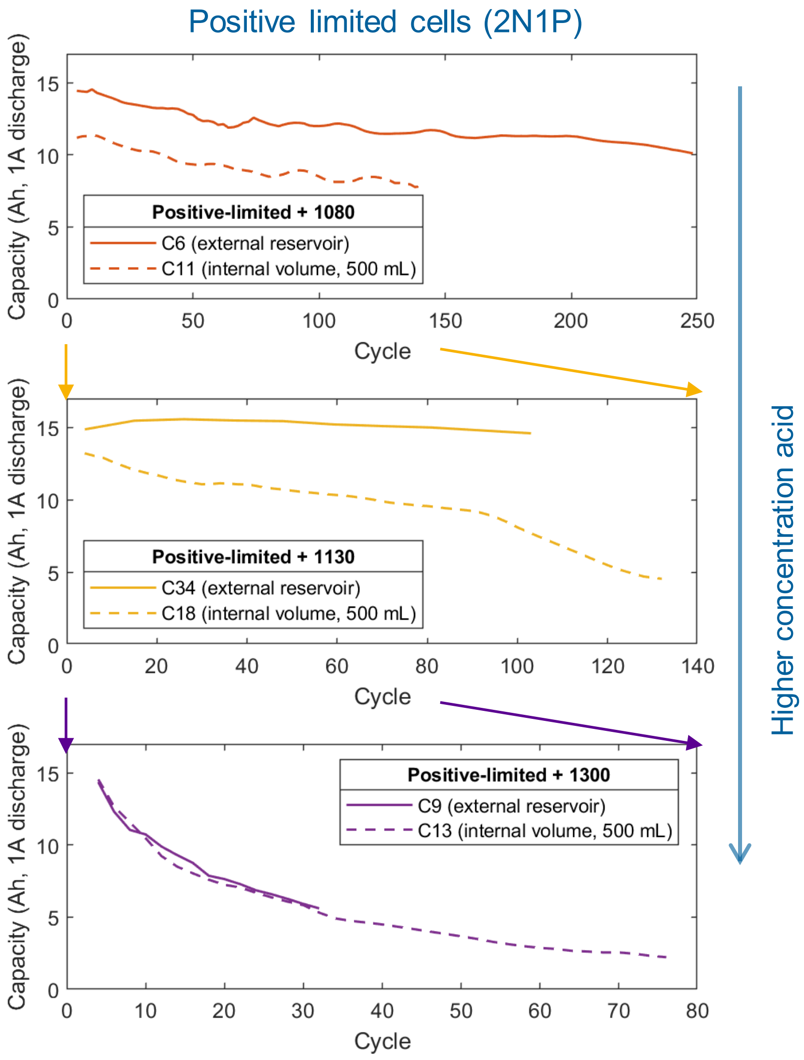
Examples of cell testing using commercial plates and modified acid handling

RESULTS

SLI plate studies

- SLI batteries NOT designed for deep cycling:
  - 10Ah plates (50% utilization)
  - Only ~50 cycles at 100%DOD.
- Control study: effect of acid concentration with higher acid volume.
  - **15Ah ~ 75% utilization! (+50% from rated value)**
  - No compression to better understand true limits of utilization (susceptible to shedding/soft shorts).
- Cycle life largely limited by positive electrode
  - **Trend: improved cycle life at lower specific gravity (SG) acid.**



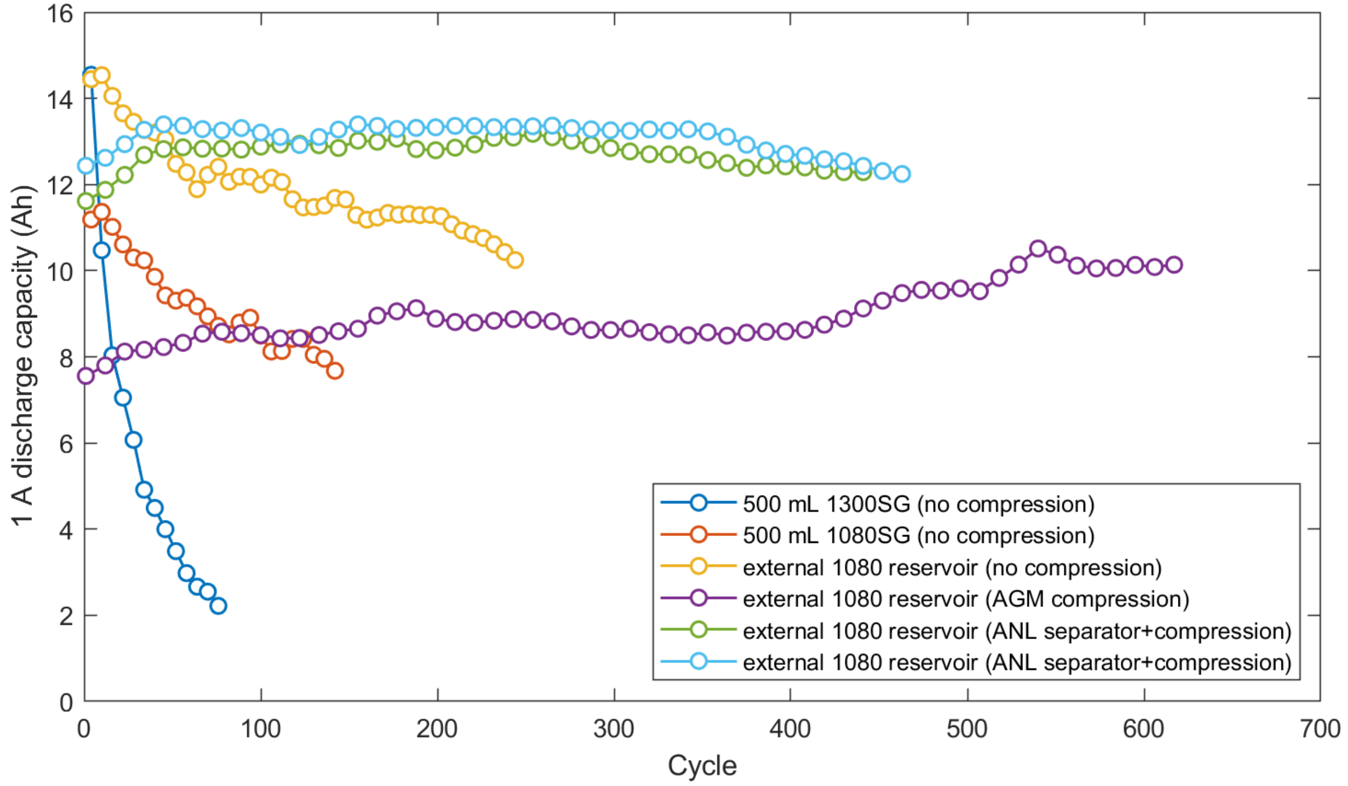


RESULTS

Low SG acid + compression (ongoing)

- Testing various compression schemes @ 100%DOD: dramatically improved cycle life.
  - Typical AGM separator with ~50% compression dramatically extends cycle life, with some loss of capacity.
  - Argonne-designed separator/cell construction: improved cycle life AND high capacity (cycle-life studies ongoing).

Results from 2N1P cycling
100%DOD (CCCV recharge, 2.5 V limit, 0.08 A current cutoff)



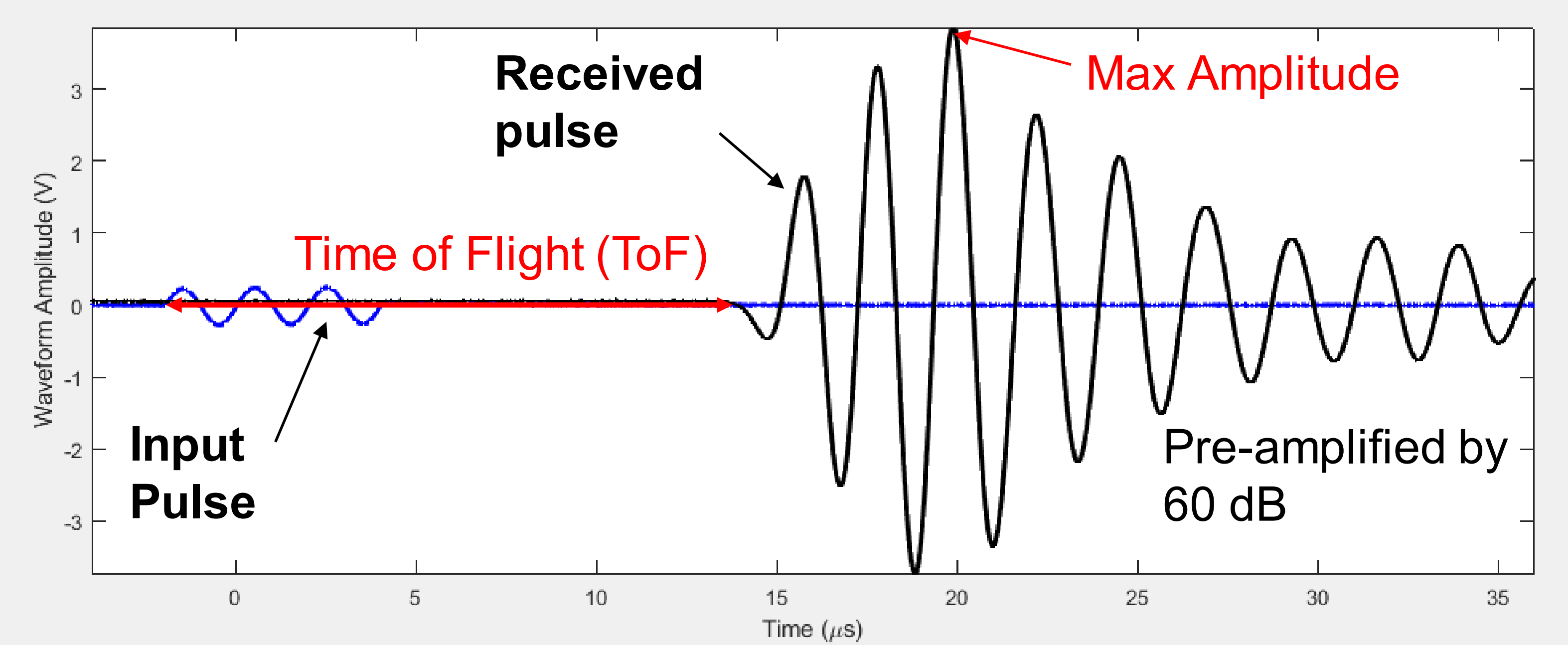
- Other tests (not shown): effect of overcharge (%), limiting voltage during charge, sealed vs. flooded, constant current/potential/voltage charging (i.e. fast charging at higher positive potential = more defects…)
- Future #1: can we further improve cycle life and RTE by optimizing SOC cycling window?
- Future #2: analyze species and charge acceptance at APS.

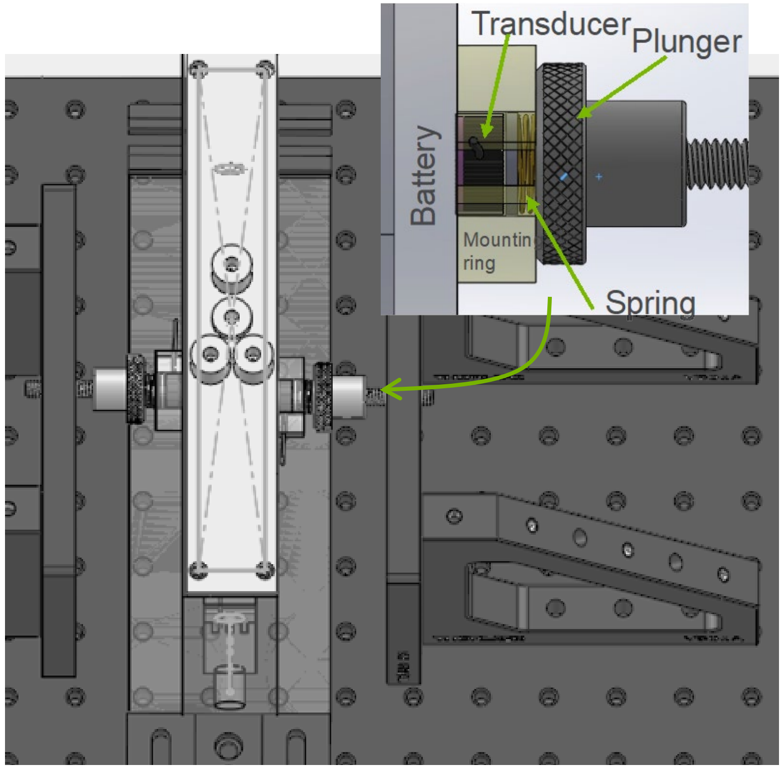
NEW TOOL: ACOUSTICS

Feedback without a synchrotron!

We increasingly need ways to evaluate local SOC and SOH.

- One approach: ultrasonic characterization.
  - Widely used in Li-ion and adapted to flow batteries (PNNL/OE).
- We have recently adapted this method to lead acid batteries.
  - Work was initiated by Sue Babinec and Tim Officer in previous industry-funded project.





Example data (left)

- Track amplitude and time-of-flight (sound velocity)
- Future: analyze waveform to extract depth-dependent information.

SOUND VS SOC

Positive/Negative Active Material

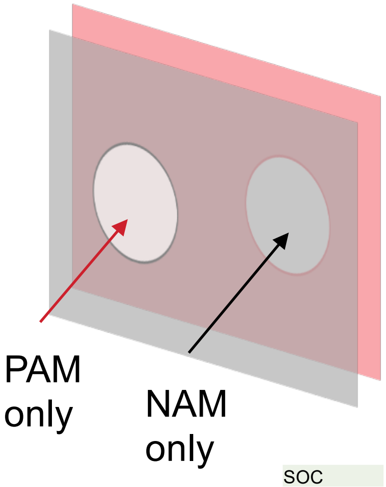
- Experiment: PSOC cycling (40-60%SOC) with holes in NAM or PAM to isolate individual electrodes.
  - Velocity response is opposite in NAM and PAM.

NAM
- Charge: slows down
- Discharge: speeds up

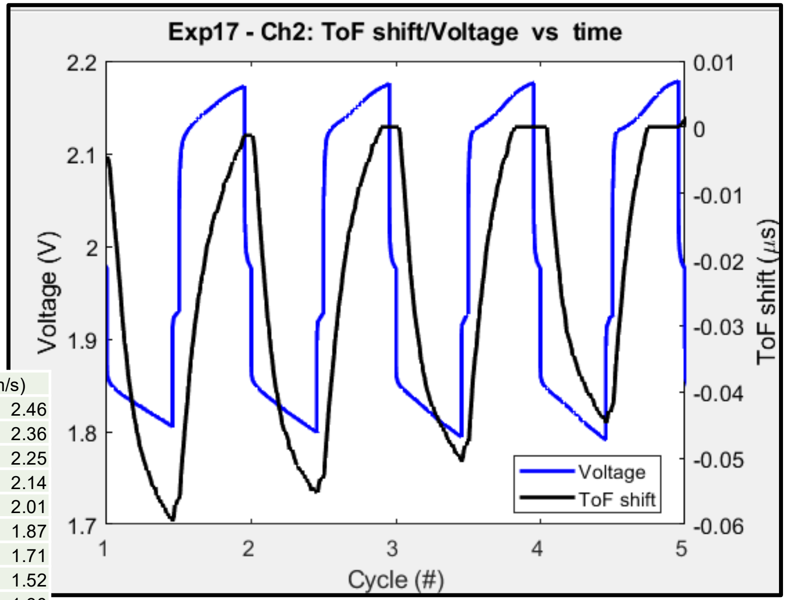
$K_{Pb} < K_{PbSO4}$

PAM
- Charge: speeds up
- Discharge: slows down

$K_{PbO2} > K_{PbSO4}$



NAM only



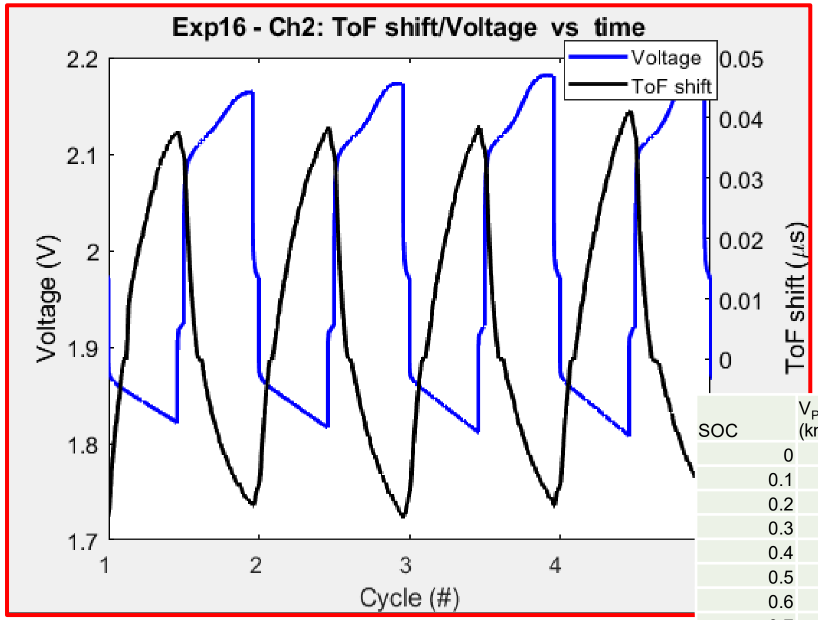
SOC	V_{NAM} (km/s)
0	2.46
0.1	2.36
0.2	2.25
0.3	2.14
0.4	2.01
0.5	1.87
0.6	1.71
0.7	1.52
0.8	1.30
0.9	1.01
1	0.58

slower ↑

$$v = \sqrt{\frac{K + \mu}{\rho}}$$

faster ↓

PAM only



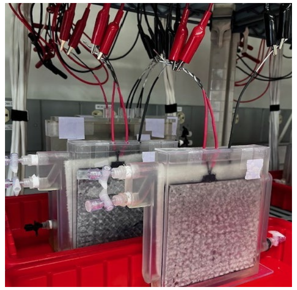
SOC	V_{PAM} (km/s)
0	2.46
0.1	2.54
0.2	2.63
0.3	2.71
0.4	2.79
0.5	2.87
0.6	2.95
0.7	3.03
0.8	3.11
0.9	3.19
1	3.27

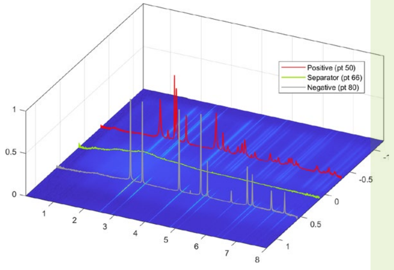
CONCLUSIONS

LEAD ACID FOR LONG DURATION

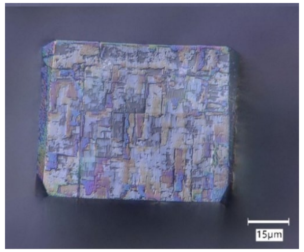
New design rules

Experiments at ANL and PNNL are providing new feedback into failure mechanisms that enables bottom-up rethinking of lead acid cell design:

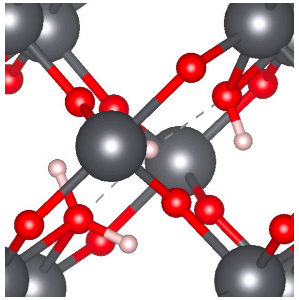




- Atomic scale: lattice defects are important for maintaining conductive, nanoscale PbO_2. Defect concentration influenced by potential and local electrolyte pH. ⟶ Overcoming positive softening/shedding with optimized charging protocols



- Particle growth: strain also affects $PbSO_4$ particle size. Can we template $PbSO_4$ via nucleation additives or dopants? ⟶ Overcoming negative sulfation with strain-engineered materials



- Electrolyte: local electrolyte concentration swings dramatically in positive electrode – can we improve utilization and life by controlling acid concentration? ⟶ Overcoming acid-limited utilization with new cell architectures

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